ARMY RESEARCH LABORATORY

Performance of Chromate-Free Pretreatment Options for CARC Systems

by Pauline Smith and Christopher Miller

ARL-TR-4049 **February 2007**

NOTICES

Disclaimers

Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5069

ARL-TR-4049 **February 2007**

Performance of Chromate-Free Pretreatment Options for CARC Systems

Pauline Smith and Christopher Miller
Weapons and Materials Research Directorate, ARL

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
February 2007	Final	1 October 2005–25 August 2006

4. TITLE AND SUBTITLE
Performance of Chromate-Free Pretreatment Options for CARC Systems

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Pauline Smith and Christopher Miller

5d. PROJECT NUMBER
AH84

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
ATTN: AMSRD-ARL-WM-MC
Aberdeen Proving Ground, MD 21005-5069

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-4049

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Chemical agent resistant coatings (CARC) are required on all tactical and support equipment. These camouflage coatings meet the survivability criteria by resisting penetration of the paint film by chemicals agents and make decontamination easier. Research efforts are primarily aimed at prevention and early detection of corrosion to maintain readiness and minimize life cycle cost. Another aspect associated with environmentally friendly coatings that are hazardous air pollutant (HAP)-free and low volatile organic compounds (VOC) is the high cost of solvents that meet the EPA criteria. Recently, the U.S. Army Research Laboratory developed a water-reducible two-component polyurethane CARC topcoat, MIL-DTL-64159, that will replace the U.S. Army's standard two-component, solvent-based CARC, MIL-C-46168. The water dispersible coating reduces VOCs by 50% and eliminates HAPs. The alternative, MIL-DTL-53039, is a solvent-borne aliphatic polyurethane that is HAP-free and low VOC. The development of these new and improved coatings have multifunctional performance requirements and need to withstand the most severe environments. Therefore, the need for effective corrosion control and detection lies at the center of our coatings research. The resistance of the coatings to corrosion was assessed using continuous exposure to salt fog per ASTM B117 and cyclic exposure per GM 9540P. Critical coating assessments including impact resistance and wet and dry adhesion were used as a basis to characterize and predict the performance of the coating. This report documents metal substrate selection, application techniques, and laboratory testing procedure.

15. SUBJECT TERMS
coatings, wash primer, primer, corrosion, DOD-P-15328D

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON / 19b. TELEPHONE NUMBER (*Include area code*)
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL	22	Pauline Smith / 410-306-0899

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Contents

List of Figures

List of Tables

1. Introduction

Chemical Agent Resistant Coatings (CARC) are required on all tactical and support equipment. These camouflage coatings meet the survivability criteria by resisting penetration of the paint film by chemicals agents and make decontamination easier. Research efforts are primarily aimed at prevention and early detection of corrosion to maintain readiness and minimize life-cycle cost. Another aspect of cost is associated with environmentally friendly coatings that are hazardous air pollutant (HAP) free and low volatile organic compounds (VOC) is the high cost of solvents that meet the EPA criteria. Recently, the U.S. Army Research Laboratory (ARL) developed a water-reducible two-component polyurethane CARC topcoat, MIL-DTL-64159 (*1*), that will replace the U.S. Army's standard two-component solvent-based CARC, MIL-C-46168 (*2*). The water dispersible coating reduces VOCs by 50% and eliminates HAPs. The alternative, MIL-DTL-53039B (*3*), is a solvent-borne aliphatic polyurethane that is HAP free and low VOC. The development of these new and improved coatings have multifunctional performance requirements and need to withstand the most severe environments. Recent studies have shown that corrosion is the major cause of downtime for critical U.S. Army assets (*4*). Therefore, the need for effective corrosion control and detection lies at the center of our coatings research. The resistance of the coatings to corrosion was assessed using continuous exposure to salt fog per ASTM B117 (*5*) and cyclic exposure per GM 9540P (*6*). Critical coating assessments including impact resistance and wet and dry adhesion were used as a basis to characterize and predict the performance of the coating. This report documents metal substrate selection, application techniques, and laboratory testing procedure.

2. Objective

The purpose of this research effort was to assess the performance of several pretreatments over traditional substrates applied with the U.S. Army coating system.

3. Experimental

The coating matrix is listed in table 1.

Table 1. Listing of substrate, pretreatment, primer, and topcoat used in this study.

Series ID	Substrate	Pretreatment	Primer	Topcoat
1	Al 2024 T3	Alodine 1200	MIL-P-53022	MIL-C-53039
2	Al 2024 T3	Alodine 1200	MIL-P-53022	MIL-DTL-64159
3	Al 2024 T3	NAVAIR TCP	MIL-P-53022	MIL-DTL-64159
4	Al 2024 T3	NAVAIR TCP	MIL-P-53022	MIL-P-53039
5	Al 2024 T3	Alodine 5700	MIL-P-53022	MIL-DTL-64159
6	Al 2024 T3	Alodine 5700	MIL-P-53022	MIL-C-53039
7	Al 2024 T3	DOD-P-15328D	MIL-P-53022	MIL-DTL-64159
8	Al 2024 T3	DOD-P-15328D	MIL-P-53022	MIL-C-53039
9	Fe 1018	None	MIL-P-53022	MIL-C-53039
10	Fe 1018	None	MIL-P-53022	MIL-DTL-64159
11	Fe 1018	Bonderite 952 P60	MIL-P-53022	MIL-DTL-64159
12	Fe 1018	Bonderite 952 P60	MIL-P-53022	MIL-C-53039
13	A1 2024 T3	None	MIL-P-53022	MIL-C-53039
14	A1 2024 T3	None	MIL-P-53022	MIL-DTL-64159
15	Fe 1018	DOD-P-15328D	MIL-P-53022	None
16	A1 2024 T3	NAVAIR TCP	MIL-P-53022	None
17	A1 2024 T3	Alodine 1200	MIL-P-53022	None
18	A1 2024 T3	Alodine 5700	MIL-P-53022	None
19	A1 2024 T3	Alodine 1200	None	None
20	A1 2024 T3	NAVAIR TCP	None	None
21	A1 2024 T3	Alodine 5700	None	None
22	A1 2024 T3	DOD-P-15328D	None	None
23	Fe 1018	Bonderite 952 P60	MIL-P-53022	None
28	A1 2024 T3	None	None	Aircraft green

4. Substrates

Two substrates were used for this project:

1. Aluminum - AL2024-T3, bare.
2. Steel, American Iron and Steel Institute (AISI) 1018, bare or treated with zinc phosphate (Bonderite B952-P60) and a chromic acid rinse.

5. Pretreatments

The CARC system application specification MIL-C-53072C (*7*) requires that metal surfaces on tactical vehicles be treated to improve adhesion and corrosion resistance prior to coating with an epoxy primer and a camouflage topcoat.

5.1 Conversion Coatings

Conversion coatings for aluminum are usually low viscosity and generally have a dry film thickness of less than one-half micron (μ). Typical coating weights are dependent on the aluminum alloy. All three pretreatments are deposited following the same traditional process used for the Alodine 1200S. The only stipulation is that silicate cleaners should not be used with the NAVAIR TCP and Alodine 5700 processes. Conversion coatings are deposited by immersion, spray, or wipe-on at ambient temperatures (75–80 °F). Depending on the condition of the metals (mill marks, ink, oil), the usual procedure is to solvent wipe or vapor degrease with acetone or methyl ethyl ketone, followed by a hot, mildly alkaline, non-silicate, non-etching aluminum cleaner. Then an acid etch and desmut are used before contact with the conversion coating solution. Better results are obtained when there is 1.5–10 min of contact time with the solution but that is dependent upon the conversion coating chosen. Alodine 1200S has the lowest pH and most active solution, therefore, it generally required the shortest reaction time of 1.5–3 min. Next, Alodine 5700 requires 3–5 min of contact with the solution while NAVAIR TCP achieves full thickness within 5 min. The contact times are longer for spray processing than for immersion processing.

1. Alodine 1200S is based on chromic acid, fluorides, and ferricyananide. The film is mostly chromium oxide/aluminum oxide. The chromium oxide in the film is about half and half trivalent and hexavalent chromium. It's one of the best treatments from a performance stand point. Alodine 1200S has a weight of 40–70 mg/ft^2 on AA-2024-T3. It was used as the control in this study.

2. NAVAIR TCP is based on zirconium fluoride and trivalent chromium sulfate; it is one of the best all-around hexavalent chromate-free alternatives. The film contains mostly zirconium oxide/aluminum oxide with ~3–5% by weight trivalent chromium and complexes with the zirconium compound. NAVAIR TCP has a coating weight of 30–50 mg/ft^2 on AA-2024-T3.

3. Alodine 5700 is based on zirconium oxide and titanium fluoride; it's one of the best non-chrome conversion coatings. It's an adhesion promoter that must be coated to offer corrosion protection. The film is mostly zirconium oxide/titanium oxide/aluminum oxide. Alodine 5700 has a coating weight that is usually below 15 mg/ft^2.

Zinc phosphate is a conversion coating for steel. In original equipment manufacturer (OEM) processes, the surface treatment is generally performed by a five-stage immersion process as prescribed in TT-C-490 (*8*). Prior to coating application, surfaces are cleaned to remove all greases, oils, and friable material using appropriate methods. In the Bonderite process, a grain refiner (or primer) is used to prepare the surface, zinc phosphate crystals are grown on the metal surface,and the surface is sealed with a finishing rinse. The coating weight must be between 150 and 500 mg/ft^2. The panels used in this study came from ACT Laboratories and were Bonderite B952 with a P60 rinse.

5.2 Wash Primer

The current pretreatment (wash primer) is DOD-P-15328D (*9*). It is formulated as a low-solid, solvent-base, containing polyvinyl butyral, phosphoric acid, and zinc chromate. Its primary function is to promote adhesion and minimize corrosion. Wash primers are cross-linked coatings applied directly to the substrate at thicknesses of 0.3–0.5 mil (1 mil = 0.001 in).

The purpose of the DOD-P-15328D wash primer is to enhance corrosion resistance through the passivation of the metal surface. In the U.S. Army's CARC system, the metal substrate is coated with a wash primer, over-coated with an epoxy primer, followed by a camouflage urethane topcoat. Several coating procedures specify the use of the wash primer, DOD-P-15328D, as a surface treatment prior to the application of an epoxy primer and polyurethane topcoat CARC system.

5.3 Primers

MIL-P-53022 (*10*) is the current solvent-based, epoxy primer, formulated with corrosion inhibiting pigments. This specification covers a flash drying, corrosion inhibiting epoxy primer for ferrous and nonferrous metals. The primer is lead and chromate free and meets the air pollution requirements for solvent emissions. Although not used in this study, MIL-P-53030 (*11*) is a water dispersible epoxy primer that is also lead and chromate free.

5.4 Topcoats

MIL-DTL-64159, type II, is a water-dispersible, aliphatic polyurethane coating formulated with a novel pigment package that uses polymeric beads as flattening agents. It is the finish coat on all military tactical equipment including ground, aviation and related support assets. The materials are free of HAPs, lead, hexavalent chromate, and have a maximum VOC content of 220 g/L (1.8 lb/gal) as packaged.

MIL-C-53039 (*12*) is the single-component, solvent-based CARC, an aliphatic polyurethane coating. It is used as a finish coat on military combat equipment. The coating is lead and hexavalent chromium free and has a maximum of 180 g/L (1.5 lb/gal) volatile organic compounds with zero volatile HAPs.

6. Accelerated Corrosion Testing

Accelerated corrosion testing was performed using both a neutral salt-spray test per ASTM B 117 and a cyclic corrosion test per GM 9540P. Salt-spray resistance is widely used by the paint industry as a quality control test and is not necessarily indicative of long-term performance of a coating. GM Standard Test 9540P is an accelerated cyclic corrosion test that was developed by

the automotive industry to more accurately replicate long term outdoor performance of coatings than the conventional salt fog test. A cyclic corrosion test chamber was used to perform the GM 9540P test. The test consists of the repetition of 18 separate stages including salt (1.25% by mass: 0.9% NaCl, 0.1%$CaCl_2$, 0.25% $NaHCO_3$) water mist, humidity, drying, ambient, and heated drying. The environmental conditions and duration of each stage for one complete GM 9540P cycle are given in table 2. Exposure to 80 cycles of a scribed panel is claimed by industry to be equivalent to 10 years of field exposure in south Florida. In addition, standard plain carbon steel calibration coupons described in GM Standard Test 9540P and supplied by GM were initially weighed and subsequently monitored for mass loss at intervals set by the specification. Mass losses measured for steel coupons used for this test were within parameters stated in the GM specification.

Table 2. GM 9540P cyclic corrosion test details.

Interval	**Description**	**Interval Time (min)**	**Temperature (±3 °C)**
1	Ramp to salt mist	15	25
2	Salt mist cycle	1	25
3	Dry cycle	15	30
4	Ramp to salt mist	70	25
5	Salt mist cycle	1	25
6	Dry cycle	15	30
7	Ramp to salt mist	70	25
8	Salt mist cycle	1	25
9	Dry cycle	15	30
10	Ramp to salt mist	70	25
11	Salt mist cycle	1	25
12	Dry cycle	15	30
13	Ramp to humidity	15	49
14	Humidity cycle	480	49
15	Ramp to dry	15	60
16	Dry cycle	480	60
17	Ramp to ambient	15	25
18	Ambient cycle	480	25

Our test used 10 panels for each coating combination in each of the accelerated tests. A single vertical scribe was made through the coating within one inch of the left edge on all but the panels with pretreatment only. Images of representative panels for each product were taken prior to exposure. Exposure to standard 5% NaCl salt fog per ASTM B117 was originally scheduled for 800 hr with removal of two panels taking place after every 200 hr of exposure. GM 9540P exposure lasted for up to 40 cycles, with two panels being removed following every 10 cycles of exposure. Upon removal, all panels were rinsed in deionized water, evaluated using ASTM D 1654 (*13*), had digital images taken on a flatbed scanner, and packaged for future examination.

7. Adhesion Testing

One panel from each of the primed or topcoated sets, save for the direct to metal (DTM) aircraft green topcoat, was immersed halfway in deionized water at room temperature (23 ± 5 °C) for 7 days per ASTM D 1308 02 (*14*). The panels were examined immediately upon removal and after a 24-hr recovery period for any defects such as blistering, loss of adhesion, color and gloss change. After the 24-hr recovery period, panels were tested for cross cut adhesion per ASTM D 3359 (*15*) method B. Six lines spaced 2 mm apart were cut through the coating using a cutting guide. The cutting guide was rotated 90°, and another six lines were cut through the coating leaving behind a grid with 25 squares cut into the coating. Standard pressure-sensitive Permacel tape was applied to the grid and removed evenly 90 s later. Testing was performed twice on each panel. Results from the immersed region were reported as wet adhesion and results from the non-immersed region were reported as dry adhesion.

Upon completion of ASTM B 117 exposure, panels were exposed to deionized water at room temperature (23 ± 5 °C) for 2 hr. Panels were removed, dried, and tested for cross-hatch adhesion as described. Every attempt was made to place grid in an area that was not visibly affected by the accelerated corrosion testing. Testing was performed twice on each panel and the average of four readings was reported for each panel set.

8. Results

The results from GM 9540P exposure are presented in table 3. It should be noted that each rating represents the performance of a single panel at a one point in time and that no panel is represented by multiple entries in this table. As a result, it is possible for a coating to have a lesser rating at one time and a better rating after a longer exposure.

For aluminum, the DOD-P-15328D outperforms all other pretreatments when no other coating is used, followed closely by NAVAIR TCP and Alodine 1200. The Alodine 5700 lasted less than 20 cycles in GM 9540P. The addition of MIL-P-53022 primer improved the overall performance of NAVAIR TCP, Alodine 1200, and Alodine 5700 but not their performance relative to one another. A complete system including MIL-P-53022 and MIL-C-53039 was insufficient protection when applied directly to the substrate. Using DOD-P-15328D as a pretreatment slightly improved the performance with the topcoated system. Using Alodine 5700 with a topcoated system demonstrated a performance improvement over the DOD-P-15328D system and over the Alodine 5700 with primer only. When MIL-DTL-64159 is used as the topcoat instead of MIL-C-46168, there is little consistent change in the performance between the two

Table 3. Performance in GM 9540P. Series have been regrouped.

Series ID	Substrate	Pretreatment	Primer	Topcoat	ASTM D 1654 Rating							
					10 Cycle		20 Cycle		30 Cycle		40 Cycle	
19	Al 2024 T3	Alodine 1200	None	None	9	9	7	7	7	7	6	6
21	Al 2024 T3	Alodine 5700	None	None	1	1	0	0	0	0	0	0
20	Al 2024 T3	NAVAIR TCP	None	None	9	8	7	7	7	7	6	6
22	Al 2024 T3	DOD-P-15328	None	None	10	9	9	9	8	7	7	6
17	Al 2024 T3	Alodine 1200	MIL-P-53022	None	9	9	9	8	9	9[b]	8[a]	8[a]
18	Al 2024 T3	Alodine 5700	MIL-P-53022	None	7	6	5	5	4[b]	4[b]	4	3
16	Al 2024 T3	NAVAIR TCP	MIL-P-53022	None	9	9	9	8	9	9	8	8
13	Al 2024 T3	None	MIL-P-53022	MIL-C-53039	8	4	4[b]	4[b]	3[b]	3[b]	2[b]	0[b]
1	Al 2024 T3	Alodine 1200	MIL-P-53022	MIL-C-53039	10	9	9	9	9	9	9	9
6	Al 2024 T3	Alodine 5700	MIL-P-53022	MIL-C-53039	8	8	9	6	6	5	4	4
4	Al 2024 T3	NAVAIR TCP	MIL-P-53022	MIL-C-53039	9	9	9	9	9	8	8	8
8	Al 2024 T3	DOD-P-15328	MIL-P-53022	MIL-C-53039	8	7	6	5	6	7	4	3
14	Al 2024 T3	None	MIL-P-53022	MIL-DTL-64159	5	4	4[b]	3[b]	3[b]	3[b]	1[b]	1[b]
2	Al 2024 T3	Alodine 1200	MIL-P-53022	MIL-DTL-64159	9	9	9	9	9	9[a]	9	9
5	Al 2024 T3	Alodine 5700	MIL-P-53022	MIL-DTL-64159	9	3	5	3	5	4	3	1
3	Al 2024 T3	NAVAIR TCP	MIL-P-53022	MIL-DTL-64159	9	9	9	8	9	7	8	6
7	Al 2024 T3	DOD-P-15328	MIL-P-53022	MIL-DTL-64159	10	5	5	4	6	5	5	2
28	Al 2024 T3	None	None	Aircraft green	8	6	8	8	7	4	7	7
15	Fe 1018	DOD-P-15328	MIL-P-53022	None	6	6	6[a]	5	5	4	4	4
23	Fe 1018	Bonderite 952 P60	MIL-P-53022	None	7	7	7[a]	6[a]	6	6	6	5
9	Fe 1018	None	MIL-P-53022	MIL-C-53039	6	6	5	5	5	4	4	3
12	Fe 1018	Bonderite 952 P60	MIL-P-53022	MIL-C-53039	8	8	8	8	7	7	7	7
10	Fe 1018	None	MIL-P-53022	MIL-DTL-64159	7	7	6	5	5	5	5	4
11	Fe 1018	Bonderite 952 P60	MIL-P-53022	MIL-DTL-64159	8	7	8	7	7	7	7	7

Note: Ratings for each interval are made on different panels.
[a]Blisters in unscribed region.
[b]Severe edge blistering.

topcoats or in the relative performance rankings of the pretreatments except for that of Alodine 5700. In this case, Alodine 5700 performed better with the MIL-C-53039. Results after 40 cycle exposure can be seen in figure 1.

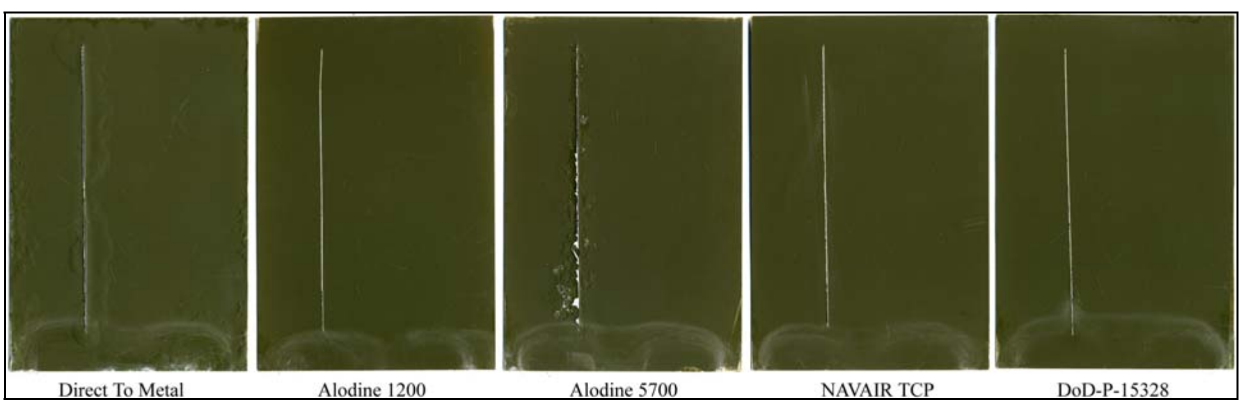

Figure 1. Al 2024 with MIL-P-53022 and MIL-DTL-64159 following 40 cycle GM 9540.

For steel, zinc phosphate with a chromate final rinse outperformed MIL-P-15328 with MIL-P-53022 and DTM (no pretreatment) with primer and topcoat. Performance of the zinc phosphate panels was improved by addition of topcoat (figure 2), although the choice of topcoat did not significantly affect performance.

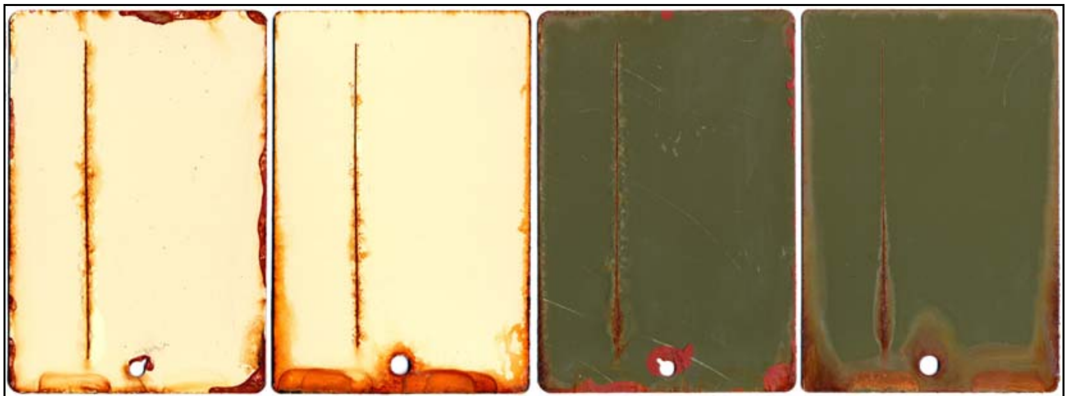

Figure 2. Steel panels with MIL-P-53022 over DTM and bonderite and MIL-C-53039 system over DTM and bonderite following 40 cycle GM 9540.

The results following exposure to ASTM B 117 are presented in table 4. As was the case for GM 9540, each rating point represents the performance of a single panel at a one point in time and that no panel is represented by multiple entries in this table. As a result, it is possible for a coating to have a lesser rating at one time and a better rating after a longer exposure.

For aluminum, the DOD-P-15328D outperforms all other pretreatments when no other coating is used when exposed to salt fog. This was the only pretreatment that had passing ratings upon completion of the exposure. Alodine 1200 was followed by NAVAIR TCP each displaying poor corrosion resistance when uncoated. The uncoated Alodine 5700 survived less than 200 hr in ASTM B 117. The addition of MIL-P-53022 primer improved the overall performance of all the pretreatments to which it was applied. The primer with Alodine 5700 continued to show poor corrosion resistance. A complete system including MIL-P-53022 and MIL-C-53039 was insufficient protection when applied directly to the substrate. Using a complete system with DOD-P-15328D slightly improved the performance of a similarly prepared substrate without topcoat and primer. Using Alodine 5700 with a topcoated system demonstrated a performance improvement over similarly prepared panels without topcoat. Alodine 1200 with waterborne topcoat and NAVAIR TCP with either topcoat experienced a slight degradation in performance over the pretreatment/primer combination. The DTM using aircraft green MIL-C53039 showed good performance before it completely failed at 800 hr. Results after 800 hr can be seen in figure 3.

Table 4. Performance in ASTM B117. Series have been regrouped.

Series ID	Substrate	Pretreatment	Primer	Topcoat	ASTM D 1654 Rating							
					200 hr		400 hr		600 hr		800 hr	
19	Al 2024 T3	Alodine 1200	None	None	6	6	7	6	5	5	4	4
21	Al 2024 T3	Alodine 5700	None	None	0	0	0	0	0	0	0	0
20	Al 2024 T3	NAVAIR TCP	None	None	7	7	5	5	4	4	3	3
22	Al 2024 T3	DOD-P-15328	None	None	10	10	10	10	8	8	8	7
17	Al 2024 T3	Alodine 1200	MIL-P-53022	None	9	9	9	9	9	9	9	8
18	Al 2024 T3	Alodine 5700	MIL-P-53022	None	8	5	7	6[b]	5[b]	5[b]	5[a]	4[b]
16	Al 2024 T3	NAVAIR TCP	MIL-P-53022	None	9	8	9	9	8	8	8	7
13	Al 2024 T3	None	MIL-P-53022	MIL-C-53039	7	6	9[b]	6[b]	6[b]	5[b]	5[b]	5[b]
1	Al 2024 T3	Alodine 1200	MIL-P-53022	MIL-C-53039	9	9	9	9	9	8	9	8
6	Al 2024 T3	Alodine 5700	MIL-P-53022	MIL-C-53039	8	7	7	7	8[b]	7[b]	7[b]	5[b]
4	Al 2024 T3	NAVAIR TCP	MIL-P-53022	MIL-C-53039	9	7	8	7	8	6	8	6
8	Al 2024 T3	DOD-P-15328	MIL-P-53022	MIL-C-53039	10	9	9	9	9	9	9	8
14	Al 2024 T3	None	MIL-P-53022	MIL-DTL-64159	8	7	5[b]	3[b]	7[b]	2[b]	7[b]	5[b]
2	Al 2024 T3	Alodine 1200	MIL-P-53022	MIL-DTL-64159	9	9	9	8	8	7	8	7
5	Al 2024 T3	Alodine 5700	MIL-P-53022	MIL-DTL-64159	8	8	8	7	4[b]	3[b]	5[b]	4[b]
3	Al 2024 T3	NAVAIR TCP	MIL-P-53022	MIL-DTL-64159	8	8	9	8	8	6	7	7
7	Al 2024 T3	DOD-P-15328	MIL-P-53022	MIL-DTL-64159	10	10	9	9	9	8	8	8
28	Al 2024 T3	None	None	Aircraft green	9	8	9	8	9	9	0	0
15	Fe 1018	DOD-P-15328	MIL-P-53022	None	7	7	6	6[a]	5[a]	5[a]	4[a]	3[a]
23	Fe 1018	Bonderite 952 P60	MIL-P-53022	None	7[a]	7[a]	7[a]	6[a]	7[a]	4[a]	5[a]	5[a]
9	Fe 1018	None	MIL-P-53022	MIL-C-53039	7	7	7	7	7	5	5	4[a]
12	Fe 1018	Bonderite 952 P60	MIL-P-53022	MIL-C-53039	8	8	8	7	7	7[a]	7	6
10	Fe 1018	None	MIL-P-53022	MIL-DTL-64159	7	7[a]	7	6	7	7	7	3
11	Fe 1018	Bonderite 952 P60	MIL-P-53022	MIL-DTL-64159	8	8	8[a]	7[a]	6	5	7	7[a]

Note: Ratings for each interval are made on different panels.
[a]Blisters in unscribed region.
[b]Severe edge blistering.

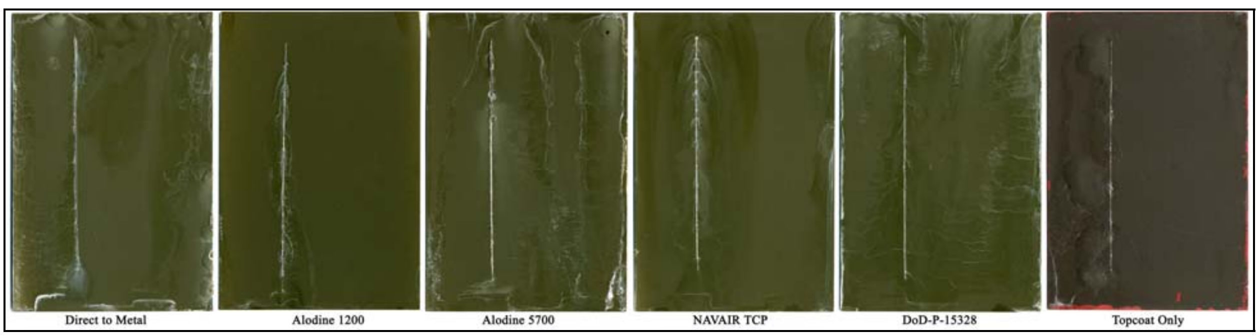

Figure 3. Al 2024 with MIL-P-53022 and MIL-DTL-64159 following 800 hr ASTM B 117.

The performance of the steel panels in ASTM B 117 was similar to though slightly worse than that of the steel in GM 9540. The Bonderite 952 outperformed the DOD-P-15328D when coated with MIL-P-53022 although blistering occurred very early on the Bonderite panels. Applying a topcoat to the Bonderite and primer system further improved performance. These systems also outperformed similar systems prepared without pretreatment. Choice of MIL-DTL-64159 over MIL-C-53039 had no consistent effect on corrosion performance. Results can be seen in figure 4.

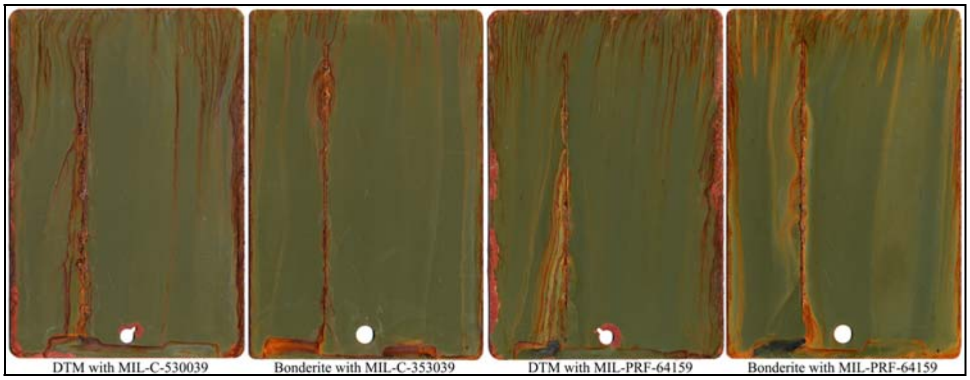

Figure 4. Steel panels with DTM or bonderite and MIL-P-53022 overcoated with MIL-C-53039 or MIL-PRF-64159 topcoat following 800 hr ASTM B 117.

As can be seen in table 5, there was little difference between the three aluminum panels with pretreatment and primer in the wet and dry adhesion tests. This changed greatly when a topcoat was added and the type of topcoat used had an impact. When using the solvent-borne MIL-C-53039, everything except the Alodine 5700 did well in the dry adhesion region. The DTM and DOD-P-15328D pretreatments suffered only slight degradation in adhesion in the immersed region vs. the dry for MIL-C-53039 topcoated panels. Alodine 1200 and NAVAIR TCP were the top performers with this system. When MIL-DTL-64159 was the topcoat, the Alodine 5700 and NAVAIR TCP were the best performers in both wet and dry adhesion. The DTM, Alodine 1200 and MIL-P-15328 performed poorly in the dry adhesion region and worse in the wet. The NAVAIR TCP had identical results for both topcoats and for both conditions.

Table 5. Cross-hatch adhesion results.

Series ID	Substrate	Pretreatment	Primer	Topcoat	ASTM D 3359 Method B Rating					
					Dry	Wet	200 hr	400 hr	600 hr	800 hr
17	Al 2024 T3	Alodine 1200	MIL-P-53022	None	5	5	5	5	4	4
18	Al 2024 T3	Alodine 5700	MIL-P-53022	None	5	5	3	3	3	3
16	Al 2024 T3	NAVAIR TCP	MIL-P-53022	None	5	4	5	4	4	4
13	Al 2024 T3	None	MIL-P-53022	MIL-C-53039	4	3	5	4	4	5
1	Al 2024 T3	Alodine 1200	MIL-P-53022	MIL-C-53039	4	4	5	5	4	4
6	Al 2024 T3	Alodine 5700	MIL-P-53022	MIL-C-53039	1	1	5	4	3	4
4	Al 2024 T3	NAVAIR TCP	MIL-P-53022	MIL-C-53039	4	4	5	4	4	5
8	Al 2024 T3	DOD-P-15328	MIL-P-53022	MIL-C-53039	4	3	5	5	5	5
14	Al 2024 T3	None	MIL-P-53022	MIL-DTL-64159	2	2	5	5	4	4
2	Al 2024 T3	Alodine 1200	MIL-P-53022	MIL-DTL-64159	3	1	5	5	4	5
5	Al 2024 T3	Alodine 5700	MIL-P-53022	MIL-DTL-64159	4	4	3	4	4	4
3	Al 2024 T3	NAVAIR TCP	MIL-P-53022	MIL-DTL-64159	4	4	4	5	3	4
7	Al 2024 T3	DOD-P-15328	MIL-P-53022	MIL-DTL-64159	3	2	4	4	4	5
15	Fe 1018	DOD-P-15328	MIL-P-53022	None	5	5	5	4	4	4
23	Fe 1018	Bonderite 952 P60	MIL-P-53022	None	4	4	5	4	3	3
9	Fe 1018	None	MIL-P-53022	MIL-C-53039	4	4	4	4	5	5
12	Fe 1018	Bonderite 952 P60	MIL-P-53022	MIL-C-53039	5	4	5	5	5	5
10	Fe 1018	None	MIL-P-53022	MIL-DTL-64159	4	4	5	5	5	5
11	Fe 1018	Bonderite 952 P60	MIL-P-53022	MIL-DTL-64159	5	5	5	5	5	5

The results were different for the wet adhesion performed following ASTM B 117 exposure. The primer over pretreatment results paralleled those from the accelerated corrosion where Alodine 1200 and NAVAIR TCP did better than the Alodine 5700. When the MIL-P-53039 was used as a topcoat for the system, DOD-P-15328D performed best, followed by NAVAIR TCP, Alodine 1200, DTM, and Alodine 5700. Alodine 5700 achieved the only low average rating of 3 out of 5 for the 600-hr condition. When the MIL-DTL-64159 topcoat was used as part of the system, the Alodine 1200 performed best. This system was followed by DTM, DOD-P-15328D, NAVAIR TCP, and Alodine 5700.

When steel was the substrate and primer was the only coating, the DOD-P-15328D slightly outperformed the Bonderite in both wet and dry adhesion. When overcoated with primer and either topcoat, Bonderite slightly outperformed the DTM process in cross hatch adhesion. The DOD-P-15328D was as good or better than the Bonderite when adhesion was tested following salt fog exposure. This was the reverse of the corrosion performance. Similarly, the adhesion results of the primer and topcoat over Bonderite and DTM were very good as compared to the mediocre salt fog corrosion performance.

9. Discussion

The pretreatment was never intended to be the sole protection of any metal surface. That said, the DOD-P-15328D performed much better than the other pretreatments in both accelerated exposures over Al 2024 T3. However, that performance was less stellar in GM 9540 when coated with primer and topcoat. The reason for this disparity is twofold; first, the wash pretreatment alone panel had a continuous coating whereas the topcoated panels had an intentional flaw (scribe) that went to the metal substrate. Second, the wash primer only panels had a much larger surface area of chromate containing coating available for corrosion passivation than did the topcoated panels (only at the scribe). The constant environment of the ASTM B 117 caused less degradation for this condition than did the GM 9540.

The addition of a MIL-P-53022 coating and a scribe through that coating improved the performance of each of the three pretreatments in both tests on Al 2024. The Alodine 1200 and NAVAIR TCP each performed well with little creep back from scribe at the end of the exposure. There was some blistering away from the scribe for the Alodine 1200 panels in the GM test. Although the performance of the Alodine 5700 improved with a primer coating, the performance was not passing the basic requirement.

Adding a topcoat to the system did not appreciably affect the performance of the Alodine 1200 in either accelerated corrosion exposure other than to eliminate the blistering seen in the GM test. The NAVAIR TCP had some degradation of performance in the constant conditions of the

ASTM B 117 but not in the GM test. The DOD-P-15328D also performed quite well in ASTM B 117. However, the performance of the coating system over wash primer degraded to an unacceptable level within 20 cycles of GM 9540. Performance of Alodine 1200 and the coating system DTM provided similar unsatisfactory results in GM 9540 and ASTM B 117. The choice of topcoat had no impact on the relative overall performance of the coating system and no consistent affect within an exposure. The aircraft green topcoat applied DTM with no primer had uneven performance over both exposures and should not be applied in that manner.

Over steel, the zinc phosphate consistently outperformed the alternative pretreatments. Using a topcoat and primer over DTM provided similar results to wash primer and primer in both accelerated exposures. Zinc phosphate with a complete system passed both exposures. Had the performance of the DOD-P-15328D improved as much as the zinc phosphate did when it was topcoated, the wash primer with a complete system likely would have passed these exposures as well.

The performance of a coating system in dry vs. wet adhesion was different in only six cases out of 19. This may be because the procedure allowed the panels to dry for 24 hr before the “wet” adhesion test was performed. The 24-hr delay makes this more of a property recovery test. As such, the panel sets topcoated with MIL-C-53039 recover the least (three out of seven) followed by MIL-PRF-64159 (two out of seven) and MIL-P-53022 (one out of five). The DOD-P-15328D was the only pretreatment to have more than one instance of performance degradation between dry and wet adhesion. All of the steel panels, the primer only aluminum, the NAVAIR TCP with either topcoat, the Alodine 1200 with MIL-C-53039 and the Alodine 5700 with MIL-DTL-64159 passed both wet and dry adhesion tests.

The relatively good adhesion results on the ASTM B 117 exposed panels can be attributed to two factors. The first is that the areas that were least affected by the accelerated corrosion test were selected for wet adhesion testing. This meant that areas whose adhesion had already been demonstrated to be good through salt fog performance were retested for a different measure of adhesion performance. Second, a 2-hr immersion time for a coating film may not have been sufficient to saturate the coating, even one that had been exposed to ASTM B 117 and allowed to dry completely. Most of the adhesion testing following ASTM B 117 exposure had passing values. The only exception on aluminum that wasn’t pretreated with Alodine 570 was NAVAIR TCP with MIL-DTL-64159 and 600 hr of salt fog. The Bonderite with MIL-P-53022 and 600 or 800 hr of salt fog were the exceptions for steel. Aside from the NAVAIR TCP, the poor performers had blistering away from the scribe which could have compromised the adhesion performance.

10. Conclusions

The performance of a pretreatment over aluminum with no additional coatings does not provide an indication of how the pretreatment will perform as part of a system. This is especially true of the pretreatments containing hexavalent chromate Cr^{+6}. The Alodine 1200 showed poor and mediocre performance in ASTM B 117 and GM 9540, respectively, when uncoated but performed well as part of a system. On the other hand, DOD-P-15328D performed well in both accelerated tests uncoated and in ASTM B 117 coated but not in GM 9540 coated.

The NAVAIR TCP performed well in all coated conditions in GM 9540. It performed nearly as well in ASTM B 117 although there were some uneven though acceptable results. The uncoated performance of NAVAIR TCP was unacceptable for ASTM B 117 and marginal for GM 9540.

The Alodine 5700 and DTM each had unacceptable performance in both accelerated corrosion tests and all coating variations.

The Bonderite had marginal-to-poor performance in all coating combinations and both accelerated tests, however, it was the best option for steel.

11. References

1. MIL-DTL-64159. *Coating, Water Dispersible Aliphatic Polyurethane, Chemical Agent Resistant* **2002**.
2. MIL-C-46168. *Coating, Aliphatic Polyurethane, Chemical Agent Resistant* **1993**.
3. MIL-DTL-53039B. *Coating, Aliphatic Polyurethane, Single Component, Chemical Agent Resistant—Supersedes MIL-E-53039A* **2005**.
4. Challener, C. Government Coatings Research: Fundamental to Performance. JCT Coatings Tech, 32–34, June 2005.
5. ASTM B 117. American Society for Testing and Materials. Standard Method of Salt Spray (Spray) Testing. *Annu. Book ASTM Stand.* **1990**, Philadelphia, PA.
6. General Motors Engineering Standard GM-9540P. *Accelerated Corrosion Test* **1997**, Detroit, MI.
7. MIL-P-53072C. *Chemical Agent Resistant Coating, (CARC) System Application Procedures and Quality Control Inspection* **1992**.
8. TT-C-490. *Chemical Conversion Coatings and Pretreatments for Ferrous surfaces* **2002**.
9. DOD-P-15328D. *Primer (Wash), Pretreatment Formula No. 117 for Metals.* Federal Specifications, **2001**.
10. MIL-P-53022. *Primer, Epoxy Coating, Corrosion Inhibiting, Lead and Chromate Free* **1988**.
11. MIL-P-53030. *Primer Coating, Epoxy, Water Reducible, Lead and Chromate Free* **2006**.
12. MIL-C-53039. *Coating, Aliphatic Polyurethane, Single Component, Chemical Agent Resistant* **2005**.
13. ASTM D 1654. American Society for Testing and Materials. Standard Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments. *Annu. Book ASTM Stand.* **1984**, Philadelphia, PA.
14. ASTM D 1308 02. American Society for Testing and Materials. Standard Test Method for Effect of Household Chemicals on Clear and Pigmented Organic Finishes. *Annu. Book ASTM Stand.* **2002**.
15. ASTM D 3359. American Society for Testing and Materials. Standard Test Method for Measuring Adhesion by Tape Test. *Annu. Book ASTM Stand.* **1998**, Philadelphia, PA.

NO. OF COPIES	ORGANIZATION
1 (PDF ONLY)	DEFENSE TECHNICAL INFORMATION CTR DTIC OCA 8725 JOHN J KINGMAN RD STE 0944 FORT BELVOIR VA 22060-6218
1	US ARMY RSRCH DEV & ENGRG CMD SYSTEMS OF SYSTEMS INTEGRATION AMSRD SS T 6000 6TH ST STE 100 FORT BELVOIR VA 22060-5608
1	DIRECTOR US ARMY RESEARCH LAB IMNE ALC IMS 2800 POWDER MILL RD ADELPHI MD 20783-1197
3	DIRECTOR US ARMY RESEARCH LAB AMSRD ARL CI OK TL 2800 POWDER MILL RD ADELPHI MD 20783-1197

ABERDEEN PROVING GROUND

1	DIR USARL AMSRD ARL CI OK TP (BLDG 4600)

NO. OF COPIES	ORGANIZATION
	ABERDEEN PROVING GROUND
13	DIR USARL AMSRD ARL WM MC P SMITH (5 CPS) C MILLER (5 CPS) J ESCARSEGA M MAHER K CHESONIS